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THE HYDROXYL RADIATION PROBLEM AND WAYS TO SOLVE IT

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Various hypotheses are compared with data on the hydroxyl emission of the upper atmosphere that have been gathered over a period of 25 years. Basic rules for this emission are formulated, and ways for studying the still unresolved aspects of the problem are evaluated. Problems, which cannot be solved without direct investigations at the base of the thermosphere, are enumerated.

1. Introduction. In 1947 new high-sensitivity means were successfully developed that permit recording the near infrared radiation of the night sky to 12,000 Å [1, 2]. These methods were also immediately put to use to scan the radiation of molecular oxygen, which, as was assumed, could appear at heights of about 100 km during the formation of molecules from oxygen atoms. As a result new radiation bands were found in the 6000-12000 Å region. Initially it was even assumed that there can be radiation from different vibrational levels of molecular oxygen in the $^1\Delta$ and $^1\Sigma$ states [3]. Shortly afterward, however, Meinel [4] obtained a very detailed spectrum of this radiation in the 6000-9000 Å region. He identified it as the rotational-vibrational spectrum of hydroxyl in the ground state.

Following this, Bates and Nicolet [5] and also Herzberg [6] assumed that the hydroxyl radiation is the result of the ozone-hydrogen reaction. Bates and Nicolet [5] explained the presence of hydrogen atoms by the photodissociation of water and methane vapors by ultraviolet solar radiation. In the years that followed this hypothesis became exceptionally popular [7]. The rotational-vibrational spectrum of hydroxyl was produced under laboratory conditions by means of the ozone-hydrogen reaction. The number of papers on instrumented research on the hydroxyl radiation of the earth's atmosphere was not large compared with the detailed theoretical descriptions of it in terms of the ozone-hydrogen reaction (see, for example, [5, 8-10]). It even seemed that further testing of the theoretical conclusions by observations is trivial and can only provide additional confirmation of processes already accepted.

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*Numbers in the margin indicate pagination in the foreign text.

We, however, have nevertheless doubted that the ozone-hydrogen reaction is the only possible source of hydroxyl radiation [11-21], and therefore we have not ignored the significant role of the intermediate excited products, which are either more efficiently ionized themselves or promote the appearance of nitric oxide molecules with a lower ionization threshold. Moreover, it seemed to us that the appearance of atomic hydrogen can be related not only to ultraviolet solar radiation directly, as Bates and Nicolet have said [5], but also to excited states of atomic and molecular oxygen, appearing during the recombination processes themselves. The identification of the hydroxyl radiation reinforced even more our initial assumptions that the infrared radiation of the upper atmosphere represents the process of molecule formation from oxygen atoms at the base of the thermosphere.

To verify all that has been stated above, first of all detailed factual data on the atmospheric hydroxyl emission itself were necessary. Therefore instead of developing abstract schemes of possible processes and using them to calculate the characteristics of the upper atmosphere, we concentrated our efforts on longer and extremely time-consuming observations of this and other related emissions in the near ultraviolet, visible and near infrared spectral regions to 12000 Å. Our research resources were very limited, however, since the opinion prevailed that the nature of the hydroxyl radiation is perfectly clear and is not related to any new processes, important for upper atmosphere physics. Under such circumstances, supporting hydroxyl research was not a prime or very expedient problem. Compared with the variety of other research projects, the International Hydroxyl Program was also extremely limited and haphazard.

Nevertheless some factual data on the hydroxyl emission itself have been gathered over nearly a quarter of a century and arguments, both for and against all known hypotheses, have been weighed carefully. Therefore the time has come to analyze them in more detail, to point out all of the most likely ones and to justify the necessity and the nature of further observations on the hydroxyl radiation of the upper atmosphere.

There is now a clearly marked trend toward re-evaluating the role of the ozone-hydrogen process. For example, the last equilibrium concentrations of O_3, H, HO_2 and O in an irradiated atmosphere, recommended by Nicolet [10], are shown in Table 1. Also given in this same table are the volume yields of hydroxyl, calculated by us on the basis of the rate coefficients, recommended in [10], for the two types of reactions shown in the table at 200°K. It is quite obvious that at altitudes of 75-80 km no more than 20-25% of all the newly formed hydroxyl molecules result from the ozone-hydrogen reaction, according to the data of [10]. No great importance was attached to the trans-hydroxyl in [5] compared with [18-20]. But, in contrast to previous assumptions, in [10] Nicolet also considers the disintegration of the hydrogen-containing molecules by O ^{1}D and O ^{1}S atoms to be important. This process was first mentioned about 20 years ago [11, 14, 15].

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TABLE 1

Altitude km	$[O_3]$, cm^{-3}	$[H]$, cm^{-3}	$[O_3][H]$ k. OH*/cm^3.sec	$[HO_2]$, cm^{-3}	$[O]$, cm^{-3}	$[HO_2][O]$ k. OH*/cm^3.sec
90	$1;1·10^8$	$2,3·10^8$	$5,4·10^3$	$4,5·10^3$	$3·10^{11}$	$6·10^4$
85	$1,0·10^8$	$6,9·10^8$	$4,6·10^5$	$5,3·10^5$	$3·10^{10}$	$6,7·10^5$
80	$1,4·10^8$	$8,6·10^8$	$2,6·10^6$	$1,7·10^7$	$1,4·10^{10}$	10^7
75	$3,2·10^8$	$5,1·10^7$	$3,6·10^5$	$1,3·10^7$	$3,8·10^9$	$2,1·10^6$

2. Actual behavior of hydroxyl emission. The major results, obtained at the Zvenigorodka station of the Atmosphere Physics Institute, USSR Academy of Sciences, are briefly stated below (the main details are in the papers of N. N. Shefov [22-30]). Certain other results will be considered at the same time.

Hydroxyl radiation appears because of the dissociation energy of molecular oxygen. Its maximum photodissociation is associated with two portions of the solar ultraviolet. The radiation in the Schumann-Runge bands is absorbed at altitudes of about 40 km and creates the classical ozonosphere primarily below this level. But hydroxyl radiation is not found in this region. The Schumann-Runge continuum is absorbed near the 100-kilometer level. According to research done outside the USSR with the aid of rockets, the most intense hydroxyl radiation occurs somewhat lower at an altitude of approximately 90 km [31-35]. On the average the hydroxyl yield is characterized as 10^{12} OH cm^2/sec or 10^6 OH cm^3/sec. This yield is no smaller than the number of Schumann-Runge continuum photons absorbed. However, the highest hydroxyl yield, based on the theoretical estimates of Nicolet (see Table 1), is considerably higher than these values [10]. Moreover, it is localized well below 90 km.

The lower altitude of the hydroxyl radiation maximum, compared with the absorption maximum of the Schumann-Runge continuum, attests to the severe vertical motion of the atmosphere and to the downward transport of atomic oxygen. The hydroxyl yield is subject, however, to large variations in the order of magnitude limits. Appreciable variations occur not only during the seasons of the year, but sometimes even within a period of several hours. These variations are not the same above different locations on earth. An obvious cause is the significant shifts of the supplies of atomic oxygen from the points where they initially appeared as a result of the strong horizontal and vertical circulations of the upper atmosphere. After geomagnetic storms a region of increased hydroxyl radiation propagates from high latitudes to the equator with a velocity of ~ 10^3 cm/sec. A region of increased radio-wave absorption moves in a similar fashion with the same velocity.

Citing Hampson, Hunten [36] widely publicized the unique result, obtained by Little, according to which the initial sharp severalfold falloff in the hydroxyl radiation intensity, and then its rapid recovery, was observed during morning illumination of the atmosphere at an altitude of 80 km. Huppi and Stair [37] repeated similar observations. Although they recorded smaller variations in the radiation intensity, they were not observed to occur at the same time as illumination of the atmosphere at an altitude of 80-100 km. Blamont and his colleagues [38] obtained a similar result. The radiation attenuation we observed

can only be associated with the time at which the geometrical shadow coincides with the 60-kilometer level. No hydroxyl radiation has yet been recorded at this altitude. The observations described were made at high altitudes near the 2-μm region of the spectrum with the aid of wide-band filters. The role of scattered twilight radiation and of the altitude determination precision in these experiments is not clear. Some variations in the hydroxyl radiation intensity near morning and evening twilights have been recorded at the Zvenigorodka station by means of an apparatus with a high spectral resolution. However, this also occurs sometimes at night. The observed intensity variations are smooth in nature and do not precisely coincide with the time at which the atmosphere at altitudes of 80-100 km is illuminated. At this moment of time the possible intensity variations are not obviously outside the measurement error (i.e., 10% of the observed intensity). In the bands arising from lower vibrational levels, the rotational temperature of the hydroxyl is somewhat lower (by approximately several tens of °K) than in the bands from the highest observable levels. This may be related to the fact that the relaxation of the rotational excitation is not completed at the high vibrational levels. Rotational temperatures, ranging up to 350°K, have been recorded. However, the bands, arising through transitions from different vibrational levels, can occur at altitudes with different temperatures. In spite of appreciable variations, the rotational temperature of the low vibrational levels is higher, on the average, in the winter and lower in the summer and approximately coincides with the seasonal temperature variations near the base of the thermosphere. In the morning and in the evening the /57 rotational temperature is several tens of °K higher than at midnight.

The population of the hydroxyl vibrational levels is subject to large random variations. It is extremely significant, however, that within the measurement accuracy limits of the intensity and the theoretical radiation transition probabilities of the hydroxyl the computed populations always decrease monotonically from the low to the high vibrational levels. On the average, the relative population of the low levels is much higher in summer than in winter, and higher in the morning and evening than at midnight. The population of the vibrational levels is satisfactorily approximated by the Boltzmann distribution. On the average, the vibrational temperature is equal to 10000 and 5000°K in the winter and summer, respectively. The variations range from 3500 to 18000°K. The yield of newly formed hydroxyl molecules at all vibrational levels, and particularly at the low levels, is an order of magnitude higher in the summer than in the winter. The increase from 5000 to 10000°K in the hydroxyl vibrational temperature is accompanied, on the average, by a fivefold rise in the radiation intensity in the $0 \to 1$ O_2 $^1\Sigma$ band of the unilluminated atmosphere. The common logarithm of this intensity is satisfactorily approximated by a linear dependence on the vibrational hydroxyl temperature, which is higher in winter than in summer, on the average.

The seasonal variations of the average characteristics of the hydroxyl radiation coincide with the variation of the illumination duration of the region where it appears. At Zvenigorodka the atmosphere above 80 km is always illuminated in the summer and it lies in darkness only in the winter around midnight. (In the spring and autumn at z = 60° toward the north, at which the observations were made, the atmosphere above 80 km was illuminated during the spectral exposure.) However, the strong horizontal and vertical circulations

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of the atmosphere, depending on the local time and season of the year, preclude associating all the effects with the duration of the local illumination exclusively.

3. Characteristics of hydroxyl radiation hypotheses.

Below, the most typical hydroxyl activation and deactivation reaction chains are designated by numbers, and the individual links are denoted by letters. The absence of a zero preceding the numeral means that in a given chain importance is attached to the vibrational and other excited states. The presence of a zero denotes the converse. Vibrational excitation of molecules is denoted by asterisks. Two asterisks correspond to a higher, one asterisk - to a lower excitation. The subscripts after k - the reaction rate coefficient - and ΔE - the energy evolved in an exothermic reaction - denote the reaction to which they refer. The atom or molecule symbol within the square brackets denotes their concentration.

Hydroxyl radiation occurs in the region where $[O_2]$ is much higher than $[O]$ and $[H]$. Therefore in triple collisions O_3 and HO_2 are formed very efficiently, while O_2, OH and H_2 are not. The assumed reaction chains are listed in Table 2: at the left are those in which excitation is ignored; at the right are those in which it is not ignored; and those reactions common to both chains are shown in the middle. The (01) chain has been suggested by Bates and Nicolet [5]. Nicolet now also considers the (02) chain [10]. For a long time we have been directing our attention to the (1) [12-15] and (2) [18, 19] chains.
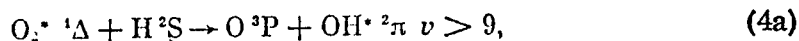
TABLE 2

$$O + O_2 + M \rightarrow O_3^* + M \quad (K = 4 \cdot 10^{-33} \text{ cm}^6/\text{sec.} \quad \Delta E = 1,1 \text{ eV}) \quad (01)\ (1)$$
$$H_2O + O \rightarrow H_2O \cdot O \quad (\alpha)$$
$$H_2O \cdot O + O_2 \rightarrow H_2O + O_3^* \quad (\beta)$$

$O_3^* \rightarrow O_3 + h\nu$ (01a)	$O_3^{*1}\Sigma + O^3P \rightarrow O_2^{*1}\Delta + O_2^{*3}\Sigma$	(1a)
$O_3^* + M (N_2, O_2) \rightarrow O_3^* + M$ (01b)	$O_3^{**1}\Sigma + O^3P \rightarrow O_3^{*1}\Sigma + O^3P$	(1b)
$O_3^{**} + O \rightarrow O_3^* + O$ (01c)	$O_3^{*1}\Sigma + H^2S \rightarrow O_2^{*1}\Delta + OH^{*2}\pi \quad v \leqslant 9$	(1c)
$O_3^{1}\Sigma + H^2S \rightarrow O_2^{*3}\Sigma + OH^{*2}\pi \quad v \leqslant 9$ (01d)	$O_2^{**3}\Sigma + O^3P \rightarrow O_2^{*3}\Sigma + O^3P$	(1d)
$O_3^{1}\Sigma + H^2S \rightarrow O_2^{3}\Sigma + OH^{*2}\pi \quad v = 9$ (01e)	$O_2^{*3}\Sigma + H^2S \rightarrow O^3P + OH^{*2}\pi \quad v \leqslant 9$	(1e)
$O_2^{**3}\Sigma + O^3P \rightarrow O_2^{*3}\Sigma + O^3P$ (01f)	$O_2^{**1}\Delta + O^3P \rightarrow O_2^{*1}\Delta + O^3P$	(1f)
$OH^{*2}\pi \quad v \geqslant 7 + O_2^{3}\Sigma \rightarrow O^3P + HO_2^{2}?$ (01g)	$O_2^{*1}\Delta + H^2S \rightarrow O^3P + OH^{*2}\pi \quad v \leqslant 9$	(1g)
	$O_2^{1}\Delta + H^2S \rightarrow O^3P + OH^{2}\pi \quad v = 0$	(1h)

$$H + O_2 + M \rightarrow HO^* + M \quad (K = 4 \cdot 10^{-32} \text{ cm}^6/\text{sec}, \quad \Delta E = 2 \text{ eV}) \quad (02)\ (2)$$
$$H_2O + H \rightarrow H_2O \cdot H \quad (\alpha)$$
$$H_2O \cdot H + O_2 \rightarrow H_2O + HO_2^* \quad (\beta)$$

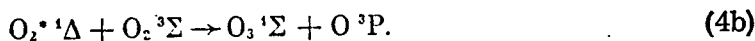|			
$HO_2^* \rightarrow HO_2 + h\nu$ (02a)	$HO_2^{*2}? + O^3P \rightarrow O_2^{*1}\Delta + OH^{*2}\pi \quad v \leqslant 9$	(2a)
$HO_2^* + M (N_2, O_2, O) \rightarrow HO_2^* + M$ (02b)	$O_2^{*1}\Delta + O^3P \rightarrow O_2^{*1}\Delta + O^3P$	(2b)
$HO_2^* + O^3P \rightarrow O_2^{*3}\Sigma + OH^{*2}\pi \quad v \leqslant 6$ (02c)	$O_2^{*1}\Delta + H^2S \rightarrow O^3P + OH^{*2}\pi \quad v \leqslant 9$	(2c)
$O_2^{**3}\Sigma + O^3P \rightarrow O_2^{*3}\Sigma + O^3P$ (02d)	$O_2^{1}\Delta + H^2S \rightarrow O^3P + OH^{2}\pi \quad v = 0$	(2d)
	$HO_2^{*2}? + H^2S \rightarrow O_2^{*1}\Delta + H_2^{*1}\Sigma$	(2e)
	$H_2^{**} + H \rightarrow H_2^* + H$	(2f)
	$H_2^* + O \rightarrow H + OH^{*2}\pi \quad v \leqslant 9$	(2g)
$OH^* \rightarrow OH + h\nu$ (03a) (3a)		
$OH + O \rightarrow O_2 + H$ (03b) (3b)		

Based on the oscillator strength [39] the lifetime of O_3^* in (01a) is greater for most vibrational levels than in (1a, b, c). The probability of the (02a) reaction is unknown. Therefore, by analogy with O_3^*, we assume that in the HO_2^* case (2a, b) are more effective than (02a).

It is erroneous to assume that only the one chain (01) guarantees OH* $v \leq 9$, while in (1) and (2) OH* certainly appear and with $v > 9$. The Wigner rule forbids the appearance of two identical O_2^* $^3\Sigma$ molecules in the (1a) reaction. But we postulate the production of a pair of O_2^* molecules with different states $^1\Delta$ and $^3\Sigma$. If some of the newly formed O_2^* $^1\Delta$ in (1a) and (2a) is so highly excited that the reaction /58

$$O_2^* \; ^1\Delta + H \, ^2S \to O \, ^3P + OH^* \, ^2\pi \; v > 9, \qquad (4a)$$

becomes possible, then the reaction

$$O_2^* \; ^1\Delta + O_2 \, ^3\Sigma \to O_3 \, ^1\Sigma + O \, ^3P. \qquad (4b)$$

will also be inevitable. The efficiency of the OH* formation in (4a) is represented by the ratio $[H]k_{4a}/([O_2 \, ^3\Sigma]k_{4b} + [H]k_{4a})$. But $[O_2 \, ^3\Sigma]$ is several orders of magnitude higher than $[H]$ everywhere in the region of hydroxyl radiation occurrence, while k_{4a} and k_{4b} are similar in value. Therefore reaction (4b) ensures the nearly total absence of OH* with $v > 9$, appearing in (4a). Otherwise, in the chain (2), even when the vibrational excitation of O_3 is very close to ΔE_1, and of HO_2 - to ΔE_2, only OH* appear with $v \leq 9$. The electron excitation energy of O_2 $^1\Delta$ reduces the maximum possible vibrational excitation by 1 eV. Therefore the excitation energy of O_2^* $^3\Sigma$ in (1a) will not exceed 4.17 eV (the dissociation energy of O_2 is equal to 5.17 eV), and of OH* in (1d) - 3.4 eV (the dissociation energy of OH is 0.77 eV less than for O_2). For the same reason the maximum energy of OH* in (2a) is limited to 3.4 eV. The excitation energy of OH* $v = 10$ is equal to 3.5 eV. Therefore the statement in [40] that the absence of OH* with $v > 9$ indicates k_{4a} exceeds k_{4b} is untenable. Because of (4b) OH* with $v > 9$ will not even occur for $k_{4a} > k_{4b}$. The ratio of the efficiencies of the (01) and (1) chains is determined by the ratio k_{4a}/k_{4b}, a precise determination of which is needed. For the present it is not clear why the k_{4b} of an atomic exchange reaction with a vibrationally excited molecule must be larger than the k_{4a} of a highly exothermic reaction between the same initial particles. But (4b) can provide some yield of unexcited O_3 $^1\Sigma$ in addition to (1b). Thus, on the basis of what has been said above only certain concentrations of unexcited O_3 can be assumed. To estimate their true values, however, other arguments or direct O_3 measurements are necessary.

If the (01g) reaction or the (02) chain were dominant, then the population of the OH* vibrational levels would be markedly reduced at $v > 6$. However, this is not observed in the actual atmospheric hydroxyl radiation. The quantity k_2 is a hundred times larger than k_1 [41, 42]. Therefore the (01) and (1) chains will not predominate over (02) and (2) for $[O] < 100[H]$. There are as yet absolutely no bases for denying such conditions exist in the region of hydroxyl radiation occurrence. The chain (2) ensures the appearance of OH* at all vibrational /59 levels from $v = 0$ to ≤ 9 when $k_{2a} > k_{02b}$.

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Polanyi and his colleagues [43] found that under laboratory conditions the reaction (1e) is accompained by the production of OH* with the maximum possible $v = 9$. They assume the subsequent deactivation of this OH* in the process

$$OH^{*\ 2}\pi_{v_{max}} + O_2{}^3\Sigma \to OH^{*\ 2}\pi_{v_{max}-3} + O_2{}^{*\ 1}\Sigma. \tag{5}$$
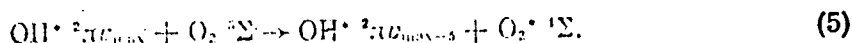
In this case the intensity of the $O_2{}^1\Sigma$ radiation should be of the order of the hydroxyl radiation intensity. In the upper atmosphere, however, at night in any case, neither predominance of OH* $v = 9$ yield nor $O_2{}^1\Sigma$ radiation of similar intensity is observed. The night time intensity of the $0 \to 0$ $O_2{}^1\Sigma$ band is about 30 kR [36], compared with 10^{12} OH cm^2/sec.

Chains (1) and (2) are characterized by the fact that in steps (1a) and (2a) one $O_2^{*\ 1}\Delta$ molecule necessarily appears. The vibrational excitation of this molecule will be quickly deactivated in its reactions with O and H. On the basis of the Wigner rule the reaction with O is forbidden only by the $O_2{}^1\Delta$ state. The reaction with H causes the complete dissociation of $O_2^{*\ 1}\Delta$ and the formation of additional OH*. If the quenching coefficient, by means of O, of the vibrational excitation of $O_2^{*\ 1}\Delta$ is of the order of 10^{-10} cm^3/sec and $[O] \approx 10^{11}$ O/cm^3, then the $O_2^{*\ 1}\Delta$ lifetime will be about 10^{-1} sec, compared with 3.6×10^3 sec for the radiation deactivation of $O_2{}^1\Delta$ [45]. Under such conditions the observation of many, although weak, $O_2^{*\ 1}\Delta$ bands is practically impossible. In principle the vibrationally excited $O_2{}^1\Delta$ can be dissociated in the (1h) and (2d) reactions. This process will be enhanced with an increase in the absolute concentration of atomic hydrogen. Unfortunately, at the present time there are no experimental values for the rate coefficient of the above-cited reaction.

The lifetime of the vibrationally excited $O_2^{*\ 3}\Sigma$ and $O_2^{*\ 1}\Delta$ molecules is equal to $1/([O]k_O + [H]k_H)$, where k_O and k_H are the rate coefficients of the reactions with O and H, respectively. Since the atomic weight of H is 16 times smaller than for O, for a given temperature $k_H \approx 4k_O$. Below we will denote $[O]/[H]$ by m. Then N_1 - the OH* yield in the (1) chain - can be represented as

$$N_1 \approx 2N \frac{[H]k_H}{[O]k_O + [H]k_H} \approx N \frac{2}{1 + 0.25m},$$

where $N = [O][O_2][M]k_1$. Similarly, in the case of the (2) process

$$N_2 \approx N + N \frac{[H]k_H}{[O]k_O + [H]k_H} \approx N \frac{2 + 0.25m}{1 + 0.25m},$$

where $N = [H][O_2][M]k_2$. For m = 100 the OH* yield in process (1) is -0.078N and in (2) -1.04N; for m = 10 in (1) it is -0.57N and in (2) -1.4N.

The quantity m is independent of the absolute O and H concentrations. Because of the strong vertical and horizontal circulation, wind shears, turbulence and infrasound vibrations of various types a severe variability in m in space and in time is inevitable in the hydroxyl radiation region. Apparently, m controls the means of OH^* formation, determining the vibrational excitation distribution with respect to different OH^* levels and, consequently, the OH^* vibrational temperature T_v also. However, it is impossible to relate, a priori, one or another m value with a certain T_v.

One possible, but not necessarily the only, hypothesis consists of the fact that in the winter the cycle (1) processes dominate for large m and T_v values. At this time an appreciable part of the O_2 dissociation energy is converted to heat, raising the temperature at the base of the thermosphere. On the other hand, in the summer the (2) cycle is more efficient since m and T_v are small.

A significant portion of the O_2 dissociation energy is removed through hydroxyl radiation. Therefore the base of the thermosphere cools. However, this does not exclude the fact that water vapor, ozone, carbon dioxide and nitric oxide may be a more efficient cooling agent than hydroxyl radiation. In this case it is still impossible to predict the connection between m and T_v. A precise determination of the OH^* yield at different vibrational levels in all the reaction chains shown in Table 2 is required, at least.

4. Molecular oxygen emissions. Observation of the $O_2\ ^1\Delta$ emission, occurring in the hydroxyl radiation region above 80 km, is possible when this region is not illuminated by solar radiation. From the work of Vallance Jones et al. [44] three well-documented cases of its observation with an intensity of $\sim 10^2$ kR are known at the present. The intensity of the analogous emission from the same, but illuminated, region amounts to about 10^3 kR according to a single determination of Hunten et al. [45]. The authors themselves explain this and the lower radiation in the illuminated region by a photodissociation of O_3. This explanation would be wholly applicable for altitudes above 80 km if there was an adequate O_3 concentration there at the time of the experiment (see below for more about this). On the basis of meager data it is very difficult to formulate a true and complete representation of the $O_2\ ^1\Delta$ emission. If, however, the data of Vallance Jones et al. [44] are most typical, then the $O_2\ ^1\Delta$ radiation is at least several times less than the average yield of $OH^* \approx 10^{12}$ OH/cm^2 · sec. This relationship may be, for example, the cause of additional $O_2\ ^1\Delta$ quenching in (1h) and (2d) by means of H (see below for information on another possible cause).

In the reaction (1a) a small amount of $O_2^{*\ 1}\Sigma$ can appear at the same time as the $O_2^{*\ 1}\Delta$. The vibrational excitations of these molecules suffer similar fates. The $O_2\ ^1\Sigma\ 0 \to 1$ emission from the unilluminated hydroxyl radiation regions can be recorded at the earth's surface. Although it cannot serve as a means for evaluating the total OH^* yield, it is quite suitable for the relative variation characteristic. It is extremely interesting that even long ago, independently of the considerations stated here, a remarkable similarity was found

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in the relative variations of some intensities and rotational temperatures of this and the hydroxyl emissions [29, 30, 46]. The decrease in the intensity at the $0 \to 1$ band of O_2 $^1\Sigma$ with a drop in T_v, more common in the summer time, serves as an indirect indication of the increase in [H], which is accompanied by an additional breakup of the O_2 $^1\Delta$ in the (1h) and (2d) reactions and by an increase in the OH* yield because of a decrease in m. In turn, an increase in this intensity with a rise in T_v, more typical of winter time, indirectly points to a decrease in [H], for which the breakup of O_2 $^1\Delta$ because of (1h) and (2d) ceases and the OH* yield decreases because of an increase in m and the process (1) activation.

The (1h) and (2d) reactions can be efficient if their rate coefficient is of the order of 3×10^{-13} cm^2/sec for [H] $\approx 10^9$ -5 $\times 10^9$ H/cm^3. An experimental determination of this quantity and long-term observations of the O_2 $^1\Delta$ emission in the unilluminated atmosphere are extremely desirable. A comparison of its rotational temperature and intensity with the intensity, rotational and vibrational temperature of the hydroxyl radiation can give very valuable information on the absence or presence of a connection between these emissions.

5. <u>Energy aspects of hydroxyl radiation.</u> For the observed radiation intensity and the corresponding OH* yield in the (01), (1), (02) and (2) reactions at least 10^6 new pairs of molecules/cm$^3 \cdot$ sec should appear. At an altitude of about 90 km [O_2] $\cdot$ [M] $\approx 7 \times 10^{26}$ molecules^2/cm^6 [47]. The values $k_1 = 4 \times 10^{-34}$ cm^6/sec and $k_2 = 4 \times 10^{-32}$ cm^6/sec are now recommended as the most reliable [41, 42]. For the yield quoted above it is necessary that [O] $\approx 3.5 \times 10^{12}$ O/cm^3 in reaction (1) and [H] $= 3.5 \times 10^{10}$ H/cm^3 in (2). These values seem to be improbable. Therefore either the yield and the OH* radiation altitude are too large, or k_1 and k_2 are too small.

The accuracy of the OH* radiation intensity measurement in the 6000-12000 Å region cannot be worse than 10%. However, the populations of the OH* vibrational levels are calculated from these intensities and the theoretical probabilities. Inaccuracy in the latter leads to a discrepancy between the calculated populations and yields and the actual. Certain circumstances cause apprehension concerning these inaccuracies.

Known absolute values of the probabilities [43-51] are too large and unequal (A $\geq$ 100 sec^{-1}). Deactivation of OH* by collisions would favor uniform population of its vibrational levels and, in the final analysis, their quenching at low altitudes. All this could facilitate understanding the monotonic filling of all vibrational levels and the observed altitude profile of the hydroxyl emission. But for the probabilities stated above this process will not be efficient. All three published (possibly not the maximum) values of the O_2 $^1\Delta$ yields in the unilluminated atmosphere are less (possibly too much) than the average OH* yield. A disagreement in the yield values is possible for small m and large k_{1h} and k_{2d}. But for large m and small k_{1h} and k_{2d} this disagreement may indicate that, in reality, either chains (1) and (2) are inefficient or the A values are incorrect. This does not exclude the fact that the too large additional hydroxyl radiation power after geomagnetic storms is also the result of using these probabilities [23, 52].

Reporduction of the hydroxyl radiation in the laboratory and the high-quality recording of its spectra in the far-infarared region are not an insurmountable problem. Therefore it is extremely desirable to replace the theoretical probabilities with experimental values.

The hydroxyl radiation altitude was determined by various authors [31-35], and we have no bases for doubting their results. The location or the time of the altitude measurements may accidentally have coincided several times with a small OH* yield. As already mentioned, this yield is subject to large random fluctuations. There is absolutely no hope in a significant increase in k_1 and k_2 [41, 42]. If, however, the OH* yield at an altitude of ~90 km is actually close to 10^{12} OH*/cm$^2 \cdot$ sec, then it must be assigned to processes such as 1α, β and 2α, β. In them it is assumed that conglomerates with a low binding energy are formed from complex molecules, such as H_2O and O and H atoms.

6. Atomic hydrogen and ozone near the lower boundary of the thermosphere. The categorical objections of Bates and his colleagues to the efficient role of vibrationally excited molecules were primarily based on the fact that the rates of atom-exchange reactions, with such molecules taking part, are of the same order as gas kinetic rates [40, 53]. These objections would be insurmountable for low [H]. But the data of Tousey and his colleagues [54] on atomic hydrogen above 90 km (~10^{12} H/cm^2) were found to be much too low since they were based on the assumption of its small optical thickness in the earth's atmosphere. Thus, the misgivings of [20], arising in connection with low [H], have become unnecessary. However, [0]/[H] is more important than [H]. There is nothing improbable even in the fact that in reality this ratio may prove to be higher than the 16:1 value previously calculated by Nicolet [10] for an altitude of 80 km.

Terrestrial observations, conducted in the Soviet Union, of the H_α hydrogen emission first discovered by us can only give an idea of the atomic hydrogen above 100 km. Its determination from the H_α intensity is less dependent on the optical thickness assumptions. The data obtained at Abastuman, where atmospheric conditions are exceptionally favorable, indicate an increase in H_α intensity toward higher latitudes and two small maximums in it in the summer and winter [55-57]. Since a considerable mass of atomic hydrogen is concentrated at high altitudes, the winter maximum can undoubtedly be due to an enrichment /62 of this region with atomic hydrogen (as well as helium) because of a transfer through the exosphere from the opposite hemisphere [58, 59]. However, the summer maximum at the time of reduced temperature at the base of the thermosphere can be considered as an indirect indicator of the increase in the influx of atomic hydrogen from lower levels, where its amount is higher in summer than in winter. Some apparent dubious correlation between the variations of H_α and OH* radiation with time at given locations had previously been reported [17, 60, 61]. This correlation cannot be observed with satellite-based measurements because of the varying dependence of these emissions on latitude and longitude [62].

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Mange [63] recently attempted to summarize the data on atomic hydrogen obtained with instruments mounted in rockets and satellites, completely ignoring earlier earth-based observations of the H_α emission. However, in examining the atomic hydrogen content at an altitude of ~ 100 km, he only made use of theoretical estimated of [H], based on abstract schemes, because of the lack of direct observations near this level.

There have been no experimental determinations of the O_3 concentration above 80 km. Hampson, based on a single result of Little's, suggested using it as a proof of ozone decomposition by solar radiation during morning twilight [36]. But at the time the OH* radiation region is illuminated, no variations exceeding the limits of the measurement accuracy occur in it. Ozone is decomposed both by ultraviolet and in reactions with H and O. The condition, defining minimin [O] and [H], masking the decomposition of O_3 by sunlight, has the form

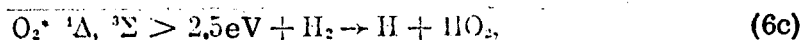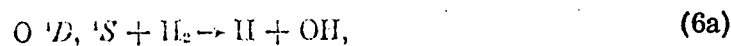$$([O, H]k + A) / [O, H]k < 1 + \Delta \quad \text{or} \quad A / [O, H]k < \Delta,$$

where [O, H] is the total concentration of O and H, k is the rate coefficient of the chemical decomposition of O_3 by these atoms, A is the probability of O_3 photodissociation by sunlight $(A = 10^{-12} \text{ sec}^{-1}$ [45]) and Δ is the relative error in the measurements of the OH* radiation intensity $(\Delta \le 10^{-1})$. For vibrationally unexcited ozone one can consider only [H] and $k = 2.5 \times 10^{-11} \text{ cm}^3/\text{sec}$ [42]. In the O_3^* case [O] will be of major importance (since [O] > [H]) with $k \approx 10^{-10} \text{ cm}^3/\text{sec}$. Thus, the minimum masking concentrations can be defined as [H] > 4×10^9 H/cm^3 for O_3 and [O] > 10^9 O/cm^3 for O_3^*. The OH* molecules can appear only because of newly formed O_3 or O_3^* molecules. The usually assumed value of $[O_3] \approx 10^8 \text{ O}_3/\text{cm}^3$ [10] provides for OH* radiation for a time of no more than 1-2 minutes. With a constant yield of newly formed O_3 and O_3^* molecules an increase in [H] and [O] is accompanied only by a decrease in $[O_3]$ and $[O_3^*]$. If OH* appear in the reaction of O_3 with H for a $10^6 \text{ O}_3/\text{cm}^3 \cdot$ sec production rate and [H] > $4 \times 10^9 \text{ H/cm}^3$, then at equilibrium $[O_3] < 10^7 \text{ O}_3/\text{cm}^3$. In the case of the reaction of O_3^* with O, however, for a similar O_3^* production rate and [O] $\approx 10^{11} \text{ O/cm}^3$, we have $[O_3^*] < 10^5 \text{ O}_3/\text{cm}^3$.

In principle, at night when there is no radiation for photodissociation, both the upward transfer of ozone and its accumulation in the hydroxyl radiation region as a result of this transfer are possible. Vallance Jones et al. [44] described an interesting behavior of $O_2 {}^1\Delta$ radiation during the night and morning hours. It was found that the illumination of the region above 80 km and even somewhat below it is not accompanied by any measurable deviation from the night time level of the intensity of this emission, undoubtedly caused, under night time conditions, by processes unrelated to the photodissociation of ozone. This means that if a change does occur because of the presence of O_3 photodissociation, it is appreciably smaller than 10^2 kR. This corresponds to an ozone content less than $10^{13} \text{ O}_3/\text{cm}^2$ or $10^7 \text{ O}_3/\text{cm}^3$.

The hydroxyl radiation problem can ultimately be resolved only on the basis of precisely determined actual data on the concentrations of O_2, HO_2, OH and, in particular, O, H and O_3. They cannot be replaced by already available predicted values [5, 8-10]. The abstract schemes that have served as the bases for calculating these concentrations are unable to explain the characteristics now known about atmospheric OH* radiation (distribution with altitude; the multitude of variations in time, space and with vibrational levels).

7. The origin of atomic hydrogen and nitric oxide. Solar ultraviolet radiation causes the formation of atomic hydrogen and nitric oxide. The $O\ ^1D$, $O\ ^1S$, $O_2^*\ ^1\Delta$ and $O_2^*\ ^3\Sigma$, appearing during recombination of oxygen atoms, greatly increase the decomposition of molecules containing hydrogen, even in the unilluminated atmosphere [11, 14, 15, 18, 19], by means of the reactions

$$O\ ^1D,\ ^1S + H_2 \to H + OH, \tag{6a}$$

$$O\ ^1S + H_2O \to 2OH, \tag{6b}$$

$$O_2^*\ ^1\Delta,\ ^3\Sigma > 2.5\,eV + H_2 \to H + HO_2, \tag{6c}$$

$$O_2^*\ ^1\Delta,\ ^3\Sigma > 3.2\,eV + H_2O \to OH + HO_2. \tag{6d}$$

The further transformation of OH and HO_2 is well known [42]. If the rate coefficients of these reactions are approximately identical, their relative efficiency can be characterized by the concentration of active, excited atoms and molecules. On the basis of nocturnal emissions, $[O\ ^1D] \ll 10^3\ O\ ^1D/cm^3$ and $[O\ ^1S] \approx 10^2\ O\ ^1S/cm^3$ [22]. If, for example, with a yield of about $10^6\ O_2^*\ ^1\Delta$, $^3\Sigma/cm^3 \cdot$ sec and $[O] \approx 10^{11}\ O/cm^3$ the $O_2^*\ ^1\Delta$, $^3\Sigma$ are deactivated at a rate of $10^{-10}\ cm^3/sec$, then $[O_2^*\ ^1\Delta,\ ^3\Sigma] \approx 10^5\ O_2^*\ ^1\Delta$, $^3\Sigma/cm^3$. These excited molecules apparently play a dominant role. A determination of the equilibrium H concentration depends on many other circumstances that have not yet been well defined, including the amount of H_2O. It is usually assumed [10] that the relative H_2O content is a constant and equal to 10^{-5}. However, the appearance of noctilucent clouds proves that at least some of the time it is much higher. Humphreys [64] in his classical work estimated it to be 1/4000. Nevertheless, many rocket determinations of H_2O appear to be too high [65]. The time and location of the generation and disappearance of atmospheric hydrogen and hydroxyl radiation are interrelated. The distribution of atomic hydrogen above the earth's radiation and its dissipation are strongly dependent on these same key circumstances.

Breig [66] recently showed theoretically that the probability of deactivation of O_2^* by O atoms increases with an increase in Δv. Consequently, very many hot oxygen atoms are formed in this process. All of them, however, immediately after formation collide almost exclusively with N_2 molecules – the

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predominant constituent of the atmosphere. A fairly significant fraction of these especially hot atoms possess energies in excess of 3.3 eV and sufficient to react, yielding NO and N. At the same time the N atoms themselves react with O_2^* and O_3^*, creating NO, O and NO, O_2. The absorption of radio waves, accompanying the region of enhanced OH* radiation after geomagnetic storms, is apparently associated with the fact that in the ionosphere D-layer additional easily ionized molecules of NO, $O_2\ ^1\Delta$ and O_2^* are created because of the flow of atomic oxygen from the polar auroral regions [13, 21, 67, 68].

8. Conclusion. Important aeronomic processes are associated with hydroxyl. Unlike the underlying classical ozonosphere, in the hydroxyl radiation region these processes are distinguished by their exceptionally large diversity, and ozone is not a typical constituent. Therefore it is impossible to consider this region only as the upper part of the classical ozonosphere, in which the role of the excited products is not great in practice. Data on the increase in   .   <u>/64</u> hydroxyl radiation after geomagnetic storms provide valuable additional information on the energy aspects of these phenomena. Therefore, further research is required for a final solution of the problems that have arisen. Terrestrial measurements are needed to determine the radiation distribution with altitude and to analyze the minor constituents.

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